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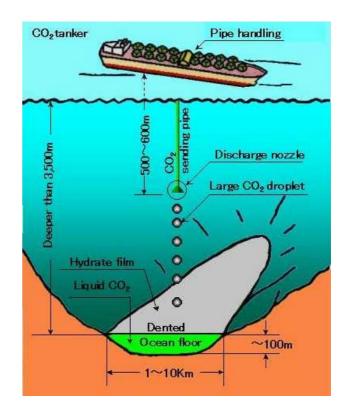
1. INTRODUCTION

In this decade, various countermeasures against the global warming have been proposed and experimentally investigated. Especially after the Third Conference of the Parties (COP-3) held in Kyoto, December 1997, the requirement to develop innovative technologies for the drastic reduction of CO₂ emission have been raised, because the achievement of Kyoto Protocol was thought difficult only by conventional measures such as energy saving.

On the other hand, in the last decade, the Ship Research Institute (SRI) had conducted various basic researches on the CO₂ storage in the ocean basin as the way to mitigate the global warming [1-12]. This measure might be promising since the sequestration term of CO₂ in the ocean is expected longer than 2000 years, the period of vertical circulation of sea water, and the ecological effects around the storage site can be limited. This method requires the deeper site than 3500 meters where liquid CO₂ becomes heavier than CO₂ saturated sea water and can be stably stored. The technical difficulties and high cost due to the deepness of its storage site, however, have been thought the disadvantages of this method.

Liquid CO2 transported by a tanker should be cooled down to -55 Celsius to reduce the tank pressure as much as possible (The triple point of CO2 is -56.6 Celsius). Such cold CO2 is heavier than sea water even in rather shallow sea. If a CO2 droplet released into 500 meters depth is lager than a certain diameter, which depend on the temperature of CO₂, it sinks to the storage site beyond 2700 meters depth where the density of CO2 in thermally equilibrium (the same temperature) is the same as that of sea water. Paying attention to this nature of cold CO2, the SRI proposed a new CO2 sending method, COSMOS (CO2 Sending Method for the Ocean Storage)[13,14], and got a Japanese patent in March 1999. The COSMOS can be expected to solve above disadvantages of storage method. Figure 1 shows the conceptual drawing of COSMOS and a cold CO2 release nozzle which is thought a breakthrough technology to realize its concept.

The temperature of liquid CO₂ released into the shallow sea is expected -45 to -30 Celsius which depends on the thermal insulation of riser tube from the CO₂ tanker. When such cold CO₂ is released into the



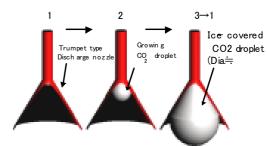


Fig. 1 Concept of COSMOS and a cold CO2 release nozzle.

Bergen, Norway, to ge sea water, a CO₂ droplet will soon be covered with ice layer and CO₂ hydrate membrane. These are expected to prevent the break up of a large droplet into small droplets but prevent the smooth and steady release of a large CO₂ droplet from the nozzle. Therefore, the technical breakthrough to realize the COSMOS is thought to be the development of CO₂ release nozzle.

Then in 1999, the SRI started an international joint research with the University of t the basic data to develop the release nozzle for cold CO2, under the auspice of the New Energy and Industrial Technology Development Organization (NEDO)[15]. In 1999, the SRI also conducted with the Monterey Bay Aquarium Research Institute (MBARI) a joint *in situ* experiment to confirm the function of trial CO2 release system. Before the *in situ* experiment, land-based experiment with mick liquid was conducted. This paper explains these land-based and *in situ* experiments.

2. TRIAL CO2 RELEASE SYSTEM

The trial release system to examine the behavior of cold CO2 in the *in situ* 500 meters deep sea is different from the real CO2 release nozzle to be developed in the future. Firstly, all CO2 contained in a tank should enough be cooled down to lower than -35 Celsius before release. Secondly, the actions to start the *in situ* release should be so simple that the robot arm equipped with the Remotely Operated Vehicle (ROV) can easily maneuver. Thirdly, total weight of the system should be less than the load limitation of the ROV (250 lbs =113 kg).

To meet above three conditions, a trial CO2 release system shown by Figure 2 was manufactured. The total weight of the system, including loaded CO2 and air as well as the framework to fix it to the ROV, is about 60 kg. The cylinder and the lid of liquid CO₂ holder have double-hull structures to keep low temperature. The volume of holder is 2.16 liters (dia: 105 mm, height: 250 mm), which means 3.0 kg of dry ice (solid CO₂) can be stored at most. The lid can be opened by only 1/8 turns. The hydraulic cylinder which pushes the piston in holder is filled by oil. The high-pressure air from two air chambers pushes down the small disc in the hydraulic cylinder. But before CO2 release, the oil in the cylinder bears up all of the downward force exerting on the small piston. The pressure of stored CO₂ is balanced with the outside pressure through oil supplied from the flexible oiler. By this means, the piston in the holder can dynamically be neutralized before CO₂ release. The neutralized piston is pushed down by making the oil in the hydraulic cylinder leak through the ball valve. The downward speed of the piston is controlled by the opening angle of the needle valve fixed on the line between the cylinder and the ball valve.

3. PROCEDURES ON BOARD

Preparations before Dive

Almost procedures on board have to be done before the ROV dives.

(1) To vacuum the double-hull space of CO₂ holder to ensure the thermal isolation.

(2) To charge high-pressure air (or N₂ gas) in two air chambers. The charging pressure is over 10 MPa. After the completion of pressurization, to close stop



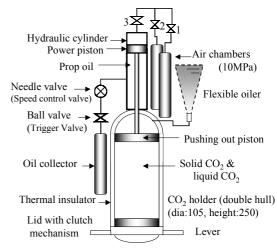


Fig. 2 Trial CO₂ release system used in the second joint *in situ* experiment with the MBARI.

valves, 1, 2 and 3.

- (3) To vacuum the oil collector.
- (4) To fill the hydraulic cylinder by oil (about 0.2 liters of turbine oil).

To set the opening angle of the needle valve which controls the downward speed of the piston.

(5) To make the system upside down.

To push the piston to the bottom of the holder. To open the lid.

To fill appropriate amount of dry ice in the holder. To close the lid by rotating the handle attached to the holder by 1/8 turns.

To connect the CO₂ charge valve to a CO₂ bottle. To pour liquid CO₂ (lower than -5 Celsius).

To make the system upright position.

(6) To fix the system to the ROV.

Two Simple Actions to Start CO2 Release

Cold CO₂ of lower temperature than -35 Celsius is liquid in the pressure equivalent to the sea deeper than 120 meters. In the concept of COSMOS, however, in order to avoid the so-called champagne phenomenon, the depth of cold CO₂ release is assumed to be deeper than 500 meters where CO₂ heated up to the temperature of sea water still remains liquid.

The actions for the ROV operator to release the cold CO₂ in the sea deeper than 500 meters should be very simple. The following two actions can initiate the CO₂ release from the trial system shown by Fig.2.

- (1) **To rotate the lid by 1/8 turns** by pulling the cord attached to the handle of the lid.
- (2) To open the ball valve by 1/4 turns.

By action (1), the lid of CO₂ holder is free to leave. But it does not fall down because the pressure in the holder balances with the pressure of sea water which is transmitted by the oil filled upside the piston. Simultaneously with start of action (2), the disc in the hydraulic cylinder and the piston in the holder are pushed down, the lid falls down and then liquid CO₂ is released into the sea water.

The main purpose of this *in situ* experiment is to confirm all functions of the manufactured trial release system and above simple actions which enables the CO₂ release in the real sea.

4. FUNCTION TEST BY A MOCK LIQUID

Before shipping the trial system to the site of *in situ* experiment, a simple experiment was conducted at the SRI to check the basic functions of the system. This experiment was done at atmospheric condition where CO2 is not liquid at any temperature, a mock liquid had been chosen. Considering thermophysical properties of fluids which seem to govern the behavior of a large cold droplet covered with ice layer, such as the density and heat capacity, as well as innocuousness, the mixture of CH₃CF₂CHCl₂ and CClF₂CF₂CHClF was selected. This chemical is sold as AK-225 by the Asahi-Kurin Ltd. Its density and the heat capacity are 1.55 gr/cc and 0.24 cal/gr, respectively.

Figure 3 shows the layout of the atmospheric mock test. Because the heat capacity of the mock liquid is

about half of liquid CO₂, the temperature of mock liquid filled in the holder is soon heated up before release into the pool water. Then the mock liquid was cooled down to $-70 \sim -80$ Celsius before being charged in the holder. The density of 1.55 gr/cc results in a large

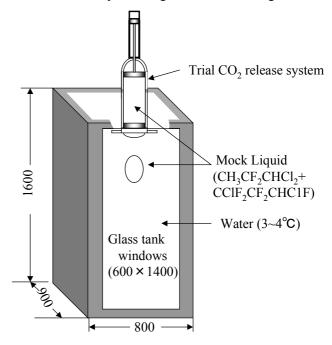


Fig.3 Layout of the atmospheric mock test for the trial CO₂ release system.



Fig.4 Monterey Bay and its vicinity.

density difference, 0.55 gr/cc, which is about 10 times larger than the case of cold (-35 Celsius) CO₂-sea water system at 500 meters depth. These differences between the mock liquid and the real CO₂-sea water system

resulted that the ice layer around released liquid was not observed and the cold mass broke up to small droplets due to rapid sinking speed.

The above-mentioned key functions of trial system were confirmed, however. And through the several tests,



Fig. 5 Main building of the MBARI who carried out the *in situ* experiment with the SRI.

the opening angle of the needle valve which controls the downward speed of piston in the CO₂ holder. Then the system was shipped to the site of *in situ* experiment, the Monterey Bay Aquarium Research Institute (MBARI), U.S.

5. SITE OF IN SITU EXPERIMENT (MBARI)

As shown by Figure 4, the Monterey Bay, looking like an ear, is about 150 km south of San Francisco. At around the root of ear, there is the famous sightseeing city, Monterey. The counterpart of the in situ experiment, MBARI, shown by Figure 5, lies in a small city, Moss Landing, which is located at the center of the ear. A very large and very steep oceanic canyon, Monterey Canyon, approaches to Moss Landing from the Pacific basin. It is possible to conduct one-day cruises for a deep ocean investigation. Then it can be said that the MBARI is located at an ideal site to conduct the in situ CO2 storage experiment. Moreover a large methane-burning power plant shown by Figure 6 stands in front of the MBARI across the state road. The shipping distance is very short if the CO₂ recovered from this power plant is used for CO2 ocean storage in the future.

The MBARI which was established by the president of Hewlett Packard Ltd., David Packard, in 1987, is a relatively new and non-governmental marine research institute. Now it has two sets of ROV. One is Ventana (mother ship: Point Lobos) for 1000 meters dive and the other is Tiburon (Western Flyer) for 4000 meters dive. It boasts of abundant image data on flora and fauna in the deep ocean.

The authors who belong to the MBARI carried out several independent *in situ* experiments for CO₂ storage in the ocean basin and found a mysterious overflow phenomenon of CO₂ hydrate [16].



Fig. 6 Methine burning large power plant standing in front of the MBARI

6. IN SITU EXPERIMENT

In November 1998, the SRI had conducted the first

joint *in situ* experiment with the MBARI to observe the fate of injected CO₂ and the effect of dissolved CO₂ on the mobile deep-sea animals (fish)[17-19]. This *in situ* experiment, the second joint activity with the MBARI, was done in October 1999. Among two ROVs owned by the MBARI, the Ventana for 1000 meters depth was used, because the depth of 500 meters is enough to confirm the functions of the trial system explained in section 2.

On the early morning of October 12, 1999, the Point Lobos left Moss Landing. It took one and half hours for the mother ship to arrive at the point to dive where the depth is about 1000 meters. Before diving, all procedures explained in section 3 were performed on bord and the trial CO2 release system was fixed to the Ventana. Figure 7 shows the Ventana just before diving. Figure 8 shows the control room where the leader of joint study (P. G. Brewer) took command of whole experiment looking several monitors, and the pilots maneuvered the ROV and the mother ship according to leader's directions. Other crew including authors in this control room also could observe the progress of experiment.

The settling down speed of Ventana is about 0.3 m/s, which means it takes 30 minutes for the ROV to arrive at the CO2 release depth (500 meters). When the ROV reached about 290 meters depth, however, some CO2 leakage through burst O ring was found. As a result of short discussions, we concluded that the leakage was caused by an over-pressure in the CO2 holder (see Fig. 2), but it relieved the over-pressure ceased after some amount of CO2 leakage. Then the diving was continued.

At the depth between 350 to 430 meters, the ROV came across a school of squid. It was seen that a red squid grasped for a while the handle of ball valve to initiate the CO2 release. The tight schedule following this CO2 release test and 10 minutes time loss due to CO2 leakage forced the authors to conduct a release test at the depth of 450 meters where CO2 heated up by sea water remains liquid in Monterey Bay.

The ROV operator succeeded in manipulating the robot arm. After two simple actions explained in section 3, the lid of CO₂ holder dropped down and liquid CO₂ was released into sea water. "Congratulations," all crew shouted. Thus, the almost functions of the trial system except CO₂ leakage were confirmed by the *in situ* CO₂ release test.

Figure 9 shows a CO₂ mass just released from the holder. As shown by Figure 10, the released liquid CO₂ mass was soon broken up into small droplets, however, and a lot of CO₂ droplets ascended in sea water. That is, a large cold CO₂ droplet did not form. It was observed through the monitor displays that some of ascending droplets were covered with hydrate membrane.

7. DISCUSSIONS

Two simple actions to initiate CO₂ release were well demonstrated in the in situ experiment. This success must be of benefit to improve the trial system for a release of cold liquid CO₂.

As the reason why CO₂ in the holder was heated up before release, it was thought that, during descendent in the sea, the turbulent flow behind the CO₂ holder, where the thermal insulation could not be



Fig. 7 ROV, Ventana, holding the CO₂ trial release release system, on the deck of Point Lobos.



Fig.8 Control room equipped with more than 10 monitor displays.

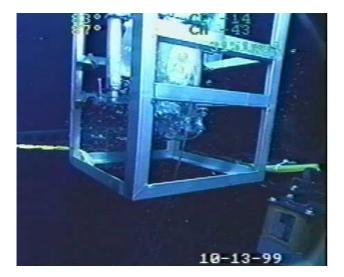


Fig.9 Single CO₂ mass released from the holder at the depth of 450 meters.

only heating up the liquid CO₂ in it but also causing an over pressure because the density of solid CO₂ is 1.4 gr/cc and its melting is followed by some volume increase.

Moreover, the fact that a large cold droplet covered with ice layer was not observed in both the function test using a mock liquid and the *in situ* experiment suggests a more sophisticated technology will be needed to develop CO₂ release nozzle, for example, the pre-water injection into cold CO₂ which is expected an enhancement of ice and hydrate formation.

At the SRI, considering above discussions as well as the experiences obtained in the function test and the *in situ* experiment, a new device to be used in the next land-based experiment for the development of cold CO₂ release nozzle is going to be designed. Figure 11 shows an example of sophisticated new device.

8. CONCLUSIONS

A land-based function test and a joint *in situ* experiment with the MBARI for a trial CO₂ release system were conducted and almost functions were confirmed to have worked well. Especially two simple actions to initiate CO₂ release *in situ* experiment could well be demonstrated. A large cold CO₂ droplet, which was also an important purpose of these experiments, however, could not observed in both experiments. This fact suggests that a more sophisticated technology will be needed to develop a CO₂ release nozzle for the COSMOS.

The SRI is under investigation of new device for the next land-based experiment and plans to conduct third joint *in situ* experiment with the MBARI in



Fig.10 A lot of CO₂ droplets broken up from a single CO₂ mass

performed due to the penetration of a pushing shaft, were unexpectedly violent. Heat inflow from sea water through this part of holder might result in not

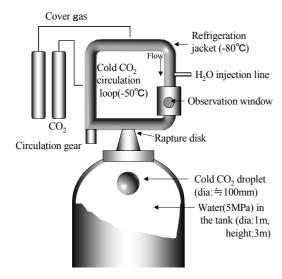


Fig.11 An example of more sophisticated new device under design at the SRI.

October, 2000 at the Monterey Bay in order to confirm the functions of the newly manufactured device.

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